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CHEMISTRY OF METHYLGALLIUM(III) COMPOUNDS IN PROTIC
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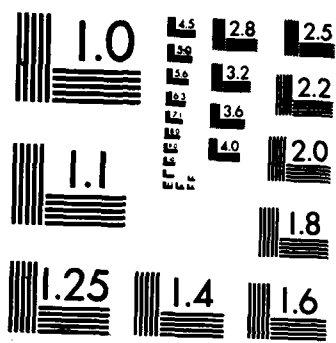
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19. ABSTRACT (continued)

by $\text{Me}_2\text{Co}(\text{BDMl}, 3 \text{ pn})$ was investigated in ethanol and acetone solutions by using UV titration and ^1H NMR data. The observed stoichiometry of the reaction requires one mol of $\text{Ga}(\text{ClO}_4)_3$ for every two mols of $\text{Me}_2\text{Co}(\text{BDMl}, 3 \text{ pn})$. The identified products are Me_2Ga^{+} and $\text{MeCo}(\text{BDMl}, 3 \text{ pn})^{+}$. In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

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Chemistry of Methylgallium(III) Compounds in Protic Solvents

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O. T. Beachley, Jr.,* R. U. Kirss, R. J. Bianchini, T. L. Royster

Abstract

The chemical properties of as well as routes to the formation of methylgallium(III) compounds in aqueous acidic solutions and in other protic solvents have been investigated. Aqueous perchloric acid solutions of $\text{Me}_2\text{GaClO}_4$ at room temperature are surprisingly resistant to hydrolytic cleavage of the gallium-carbon bond. Only 14% of the available methyl groups of $\text{Me}_2\text{GaClO}_4$ when dissolved in 0.0171 M HClO_4 are converted to CH_4 after a three month time period. In contrast, $\text{Me}_2\text{GaClO}_4$ undergoes a significantly faster methyl transfer reaction with $\text{Ga}(\text{ClO}_4)_3$ in aqueous HClO_4 solution to form $\text{MeGa}_{(\text{aq})}^{+2}$ which in turn hydrolyzes to form $\text{Ga}_{(\text{aq})}^{+3}$ and methane. Approximately 36% of the initially available methyl groups form CH_4 in three months. The dimethylgallium cation also methylates $\text{Hg}_{(\text{aq})}^{+2}$ to form $\text{MeGa}_{(\text{aq})}^{+2}$ and $\text{MeHg}_{(\text{aq})}^{+}$ in aqueous solution but $\text{Me}_2\text{Ga}_{(\text{aq})}^{+}$ does not react with $\text{Al}_{(\text{aq})}^{+3}$, $\text{Zn}_{(\text{aq})}^{+2}$ or $\text{Na}_{(\text{aq})}^{+}$. In a second series of experiments the methylation of gallium(III) by $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ was investigated in ethanol

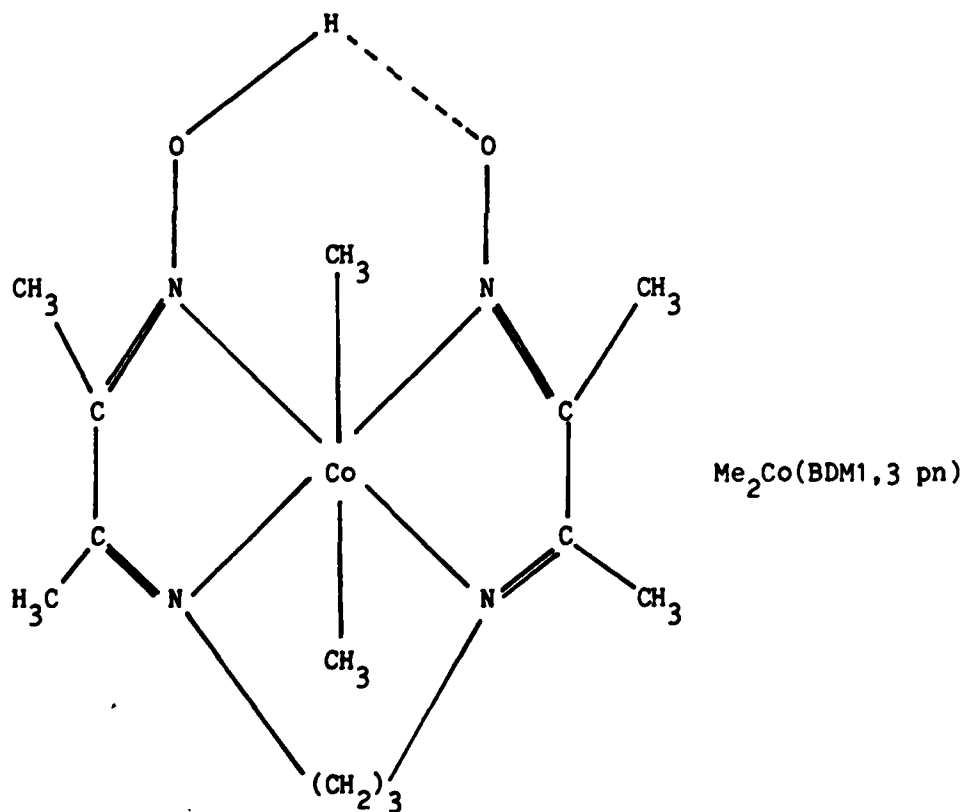
and acetone solutions by using UV titration and ^1H NMR data. The observed stoichiometry of the reaction requires one mol of $\text{Ga}(\text{ClO}_4)_3$ for every two mols of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$. The identified products are Me_2Ga^+ and $\text{MeCo}(\text{BDM1,3 pn})^+$. In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

Introduction

Methylgallium compounds can exist in aqueous solution¹ and these solutions are exceedingly toxic.^{2,3} The inorganic derivatives of gallium are also poisonous.³ However, relatively little is known about the hydrolytic stability, the chemical reactions or the modes of formation of methylgallium compounds in aqueous solution. The hydrolysis of trimethylgallium is very rapid until the first methyl group has been removed and then further hydrolysis becomes slow.^{1,4,5} The removal of the second and third methyl groups has been described as being particularly slow.^{1,4,5} For example, the reaction of a diethylether solution of $\text{Me}_3\text{GaOEt}_2$ with a slight excess of water gives Me_2GaOH , which in turn reacts readily with both aqueous acids and bases at room temperature without rupture of the gallium carbon bonds.⁵ No methane evolution⁵ was reported when either excess HNO_3 , HClO_4 or NaOH was added to Me_2GaOH . However, after the resulting solutions had been at room temperature for several hours, very small quantities of a gas were observed.⁵ No further details regarding the extent of hydrolysis or the reaction products have been described in the literature.

The presence of toxic organometallic compounds in the aqueous environment has prompted numerous studies of reactions of metal ions with a variety of methylcobalt complexes. Mercury(II),^{6,7} chromium(II)⁸ and thallium(III)⁹ have been observed to react with either [bis(diacetylmonooximeimino)1,3propane]dimethylcobalt(III) [$\text{Me}_2\text{Co}(\text{BDM1,3 pn})$] or bis(dimethylglyoximate)monomethylcobalt(III) to form MeHg^+ , MeCr^{+2} and MeTl^{+2} , respectively. Zinc(II), cadmium(II), and lead(II) also react with 2 mols of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ in isopropanol to initially form ZnMe_2 , CdMe_2 and PbMe_2 , respectively, which then rapidly hydrolyze in the reaction solvent to liberate two mols of methane per mol of metal.¹⁰

The increasing importance of methylgallium compounds to the electronics industry as well as the potential presence and impact of methylgallium compounds in the environment lead us to study the chemical properties of methylgallium compounds in aqueous solution and in protic solvents. In this paper we report the results of our investigations of the hydrolytic stability of methylgallium compounds in dilute perchloric acid solution and of methyl transfer reactions between aqueous solutions of dimethylgallium(III) cations and gallium(III), aluminum(III) and zinc(II) perchlorate salts and mercury(II) nitrate. Secondly, we report on the



methylation of gallium(III) by Me₂Co(BDM1,3 pn) in protic solvents. Our results demonstrate that aqueous solutions of dimethylgallium(III) cations are stable to hydrolysis of the gallium-carbon bond over a limited time

period but methyl transfer reactions can occur between $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ and $\text{Ga}^{+3}_{(\text{aq})}$ and $\text{Hg}^{+2}_{(\text{aq})}$. Furthermore, $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ reacts with gallium(III)perchlorate in a 2:1 stoichiometry in ethanol solution to produce Me_2Ga^+ as the only methylgallium(III) product. These reactions represent the first examples of the methylation of gallium(III) in protic solvents.

Experimental

General. All of the compounds used in these studies, with the exception of trimethylgallium diethyletherate, were handled on the laboratory bench top. Trimethylgallium diethyletherate was prepared from GaCl_3 and the methyl Grignard reagent in diethyl ether under an argon atmosphere. Dimethylgallium hydroxide was prepared from isolated and purified $\text{Me}_3\text{Ga}\cdot\text{OEt}_2$ and water in diethyl ether at room temperature.⁵ Dimethylgallium perchlorate⁵ was prepared from Me_2GaOH and HClO_4 . The cobalt complex, $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$, was prepared from $\text{Co}(\text{BDM}1,3 \text{ pn})[\text{ClO}_4]_2$ using previously published methods.^{10,11} The formation of CH_4 from the hydrolysis of methylgallium(III) compounds was confirmed after isolation by fractional vacuum distillation and identification by vapor pressure measurements at -196°C (10 mm).

Spectral Measurements. Infrared spectra were recorded in the range 4000 to 250 cm^{-1} by using either a Perkin-Elmer 457 or 683 spectrometer. Spectra of solids were observed as Nujol mulls using KBr or CsI windows. Ultraviolet spectra were recorded by using a Perkin-Elmer 575 UV-visible spectrometer and 1 cm quartz cells. Proton NMR spectra were recorded by using a Varian EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) with internal references of benzene (δ 7.13) or sodium 3-(trimethylsilyl)-1-propane sulfonate (δ 0.00). The following chemical shifts (reference benzene 7.13 ppm) of starting materials were observed: $\text{Me}_2\text{GaOH}(\text{acetone-}d_6)$ -0.56(Me,s), 4.28(H,s); $\text{Me}_2\text{Ga}(\text{ClO}_4)(\text{acetone-}d_6)$ -0.29(Me,s); $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})(\text{acetone-}d_6)$ -0.19(Me,s), 1.94(s), 1.84(m), 2.04(s), 4.52(s).

Determination of Hydrolytic Stability of $\text{Me}_2\text{GaClO}_4$ in Aqueous Solutions by Measuring the Evolved Methane. The hydrolytic stability of an aqueous

acidic solution of $\text{Me}_2\text{GaClO}_4$ was monitored by measuring the evolved CH_4 by using a Toepler pump-gas buret assembly. The following data were observed for a solution of 2.23 mL which was 0.994 M $\text{Me}_2\text{GaClO}_4$ (2.217 mmol), 0.0171 M HClO_4 and 1.27 M acetone, [Time, (mmol CH_4 , % available methyl groups converted to CH_4)]: 6 days (0.0629, 1.42), 13(0.121, 2.73), 20(0.166, 3.74), 27(0.210, 4.74), 34(0.254, 5.73), 48(0.356, 8.02), 105(0.647, 14.6).

In a second series of experiments, the methane evolved from an aqueous solution of 2.96 mL which was 1.02 M $\text{Me}_2\text{GaClO}_4$ (3.008 mmol), 0.884 M $\text{Ga}(\text{ClO}_4)_3$ (2.617 mmol), 0.0164 M HClO_4 and 1.00 M acetone was investigated. The following measurements of evolved CH_4 were observed: [Time (mmol CH_4 , % available methyl groups converted to CH_4)]: 6 days (0.157, 2.61), 13(0.336, 5.59), 20(0.478, 7.94), 27(0.610, 10.1), 34(0.761, 12.6), 48(1.12, 18.6), 76(1.93, 32.1), 103(2.22, 36.9).

Determination of Hydrolytic Stability of $\text{Me}_2\text{GaClO}_4$ in Aqueous Solution by Using ^1H NMR Spectroscopy. The hydrolytic stability of $\text{Me}_2\text{GaClO}_4$ contained in sealed NMR tubes was evaluated using ^1H NMR spectral data. For one series of experiments an aqueous solution which was 1.25 M $\text{Me}_2\text{GaClO}_4$, 0.020 M HClO_4 and 1.25 M acetone was prepared. The relative intensity of the single line due to $\text{Me}_2\text{GaClO}_4$ versus the line due to acetone was monitored over a period of 150 days. The following data were observed: Time (Integration ratio $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ /acetone): 0 days (1.0), 0.79 (0.95), 1.01 (1.0), 2.04 (0.86), 5.96 (0.96), 13.00 (0.99), 14.00 (0.96), 34.00 (0.99), 150.00 (1.0). After 150 days, an extremely small line due to $\text{MeGa}^{2+}_{(\text{aq})}$ was just barely visible in the spectrum.

For a second series of experiments an aqueous solution which was 1.12 M $\text{Me}_2\text{GaClO}_4$, 0.969 M $\text{Ga}(\text{ClO}_4)_3$, 1.12 M acetone and 0.0179 M HClO_4 was monitored over a period of 150 days. During the course of this study, the

^1H NMR line due to $\text{Me}_2\text{Ga}^+(\text{aq})$ decreased in intensity and a new line due to MeGa^{2+} appeared but never became very large relative to the line due to acetone. The following data were observed: Time (Integration ratio $\text{Me}_2\text{Ga}^+(\text{aq})/\text{acetone}$; $\text{MeGa}^{2+}/\text{acetone}$): 0 days (0.92; 0); 0.79 (0.89; 0.027); 1.01 (0.95; 0.025); 2.04 (0.90; 0.024); 5.96 (0.85; 0.063); 13.00 (0.74; 0.11); 34.00 (0.62; 0.17); 150.00 (0.042; 0.31).

In order to determine the effects of other metal perchlorate salts on the hydrolytic stability of $\text{Me}_2\text{Ga}^+(\text{aq})$, saturated aqueous solutions of $\text{Me}_2\text{GaClO}_4$ containing 0.0912 M HClO_4 were mixed with aqueous solutions of $\text{Al}(\text{ClO}_4)_3$, $\text{Zn}(\text{ClO}_4)_2$ and NaClO_4 . The ^1H NMR spectrum of these resulting solutions were monitored over a 150 day time period. The line due to $\text{Me}_2\text{Ga}^+(\text{aq})$ did not decrease in intensity and no new lines suggesting the formation of $\text{MeGa}^{2+}(\text{aq})$ or any other methylmetal species appeared.

Methyl Transfer Reactions Between $\text{Me}_2\text{GaClO}_4$ and $\text{Hg}(\text{NO}_3)_2$ in Aqueous HClO_4 Solution. The reaction between $\text{Me}_2\text{GaClO}_4$ and $\text{Hg}(\text{NO}_3)_2$ in aqueous perchloric acid was monitored by means of a ^1H NMR spectral titration. To an NMR tube which contained one ml of saturated $\text{Me}_2\text{GaClO}_4$ solution in 0.0912 M HClO_4 was added 0.173 M $\text{Hg}(\text{NO}_3)_2$ dropwise. The ^1H NMR spectrum was recorded after each Hg^{2+} addition. The data support the formation of $\text{MeGa}^{2+}(\text{aq})$ and $\text{MeHg}^+(\text{aq})$ (see Results and Discussion).

UV Spectral Titrations. Solutions of $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ in absolute ethanol (0.203 to 0.292 mM) were titrated with 4.14 mM $\text{Ga}(\text{ClO}_4)_3$ in absolute ethanol in 0.50 mL increments. The extent of reaction was monitored by following the change in the UV spectrum in the 390 to 500 nm range of a sample contained in 1-cm quartz cells after equilibrium was established. The addition of $\text{Ga}(\text{ClO}_4)_3$ was discontinued after at least three additions caused no change in the absorbance at 412 nm. The purity of $\text{Me}_2\text{Co}(\text{BDM}1,3$

pn) was verified before each titration by recording the spectrum, noting the presence of the absorption at 412 nm characteristic of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ as well as the absence of the absorption at 470 nm characteristic of $\text{MeCo}(\text{BDM1,3 pn})^+$ and calculating the extinction coefficient of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$. Similar UV titrations were studied in order to detect a potential reaction between methylcobalamin and $\text{Ga}(\text{ClO}_4)_3$ in water.

Identification by ^1H NMR Data of the Methylated Gallium Species From the Reaction of $\text{Ga}(\text{ClO}_4)_3$ with $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$. A small quantity of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ was dissolved in the desired solvent and the ^1H NMR spectrum was recorded. Then, a sample of $\text{Ga}(\text{ClO}_4)_3$ (0.50 mol/mol $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$) was added and the spectrum was recorded a second time. The appearance of lines assigned to $\text{MeCo}(\text{BDM1,3 pn})^+$, Me_2Ga^+ and/or MeGa^{+2} were noted. After the spectrum showed no further change with time, a small quantity of a known solution of $\text{Me}_2\text{GaClO}_4$ was added to verify the identity of the Me_2Ga^+ line. These studies were carried out in both acetone- d_6 and ethanol- d_6 .

Results and Discussion

Our experimental results demonstrate that aqueous acidic solutions of $\text{Me}_2\text{GaClO}_4$, which are reported⁵ to contain $\text{Me}_2\text{Ga}(\text{H}_2\text{O})_2^+$ and are represented as $\text{Me}_2\text{Ga}^+_{(\text{aq})}$, are surprisingly resistant to hydrolytic cleavage of the gallium-carbon bond to produce methane. In contrast, $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ undergoes a significantly faster methyl transfer reaction with $\text{Ga}^{+3}_{(\text{aq})}$ in aqueous HClO_4 solution to form $\text{MeGa}^{+2}_{(\text{aq})}$ which in turn hydrolyzes to form $\text{Ga}^{+3}_{(\text{aq})}$ and methane. Available data also suggest that $\text{MeGa}^{+2}_{(\text{aq})}$ hydrolyzes much more rapidly than $\text{Me}_2\text{Ga}^+_{(\text{aq})}$. The dimethylgallium cation also methylates $\text{Hg}^{+2}_{(\text{aq})}$ to form $\text{MeGa}^{+2}_{(\text{aq})}$ and $\text{MeHg}^+_{(\text{aq})}$ but $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ does not react with $\text{Al}^{+3}_{(\text{aq})}$, $\text{Zn}^{+2}_{(\text{aq})}$ or $\text{Na}^+_{(\text{aq})}$. Conversely, gallium(III) is methylated by $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ to form Me_2Ga^+ and $\text{MeCo}(\text{BDM}1,3 \text{ pn})^+$ in ethanol and acetone solution. These methylation reactions of gallium represent the first examples in which gallium-carbon bonds are formed in protic solvents, including water.

The hydrolytic stability of methylgallium cationic species in HClO_4 solution and the propensity of these cations to undergo methyl transfer reactions were monitored by measuring the evolved CH_4 and by following the changes in the ^1H NMR spectrum of related solutions. In the ^1H NMR experiments, the intensities of the lines due to $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ (-0.35 ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate) and acetone were compared for 0.02M HClO_4 solutions equimolar in $\text{Me}_2\text{GaClO}_4$ and Me_2CO . The NMR signal due to $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ did not decrease in intensity over a period of five months and no other new signals of significant intensity appeared. In the experiments in which the CH_4 was measured, only 0.0642 mmol of CH_4 was formed after 6 days from 2.217 mmol of $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ and only 0.647 mmol CH_4 was measured after 105 days, less than 15% of the available methyl groups. Both types of observations confirm that the hydrolysis of $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ in 0.02 M

HClO₄ is exceedingly slow. However, when a 0.018 M HClO₄ solution equimolar in Me₂GaClO₄, Ga(ClO₄)₃ and Me₂CO was observed over the same time period, the intensity of the ¹H NMR line due to Me₂Ga⁺_(aq) decreased with time and one new line at -0.14 ppm (referenced to sodium 3-(trimethylsilyl)propanesulfonate) due to MeGa⁺²_(aq) appeared in the spectrum, and grew slightly in intensity but never became very large relative to the acetone line. (The assignment of the new line to MeGa⁺²_(aq) is based on a comparison of the chemical shift of this line to a line in the spectrum of MeGaCl₂ dissolved in a mixture of HClO₄, acetone and water at the identical pH.) The Me₂Ga⁺_(aq) line decreased to one half of its original intensity in approximately 80 days. However, the sum of the intensities of the lines due to Me₂Ga⁺_(aq) and MeGa⁺²_(aq) decreased relative to the intensity of the internal acetone sample. In the quantitative experiments of evolved CH₄, 0.157 mmol of CH₄ was formed after 6 days from an acidic solution which initially contained 3.01 mmol of Me₂Ga⁺_(aq) and 2.617 mmol of Ga⁺³_(aq). This quantity of CH₄ is almost twice that observed for the solution which contained Me₂Ga⁺_(aq) as the only initial gallium species. Our observations are consistent with the occurrence of a methyl transfer reaction (equation 1) and the hydrolysis of the resultant MeGa⁺²_(aq) (equation 2). Thus,



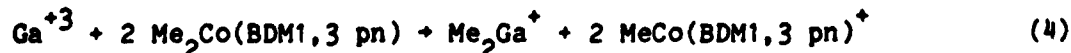
MeGa⁺²_(aq) is significantly more susceptible to gallium-carbon bond cleavage with methane formation than is Me₂Ga⁺_(aq) in aqueous perchloric acid solution.

Methyl transfer reactions also occur between $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ and $\text{Hg}^{+2}_{(\text{aq})}$ in aqueous HClO_4 solution but this reaction is significantly faster than methyl transfer between $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ and $\text{Ga}^{+3}_{(\text{aq})}$. The intensity of the ^1H NMR line due to $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ at -0.35 ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate, in a solution initially equimolar in $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ and $\text{Hg}^{+2}_{(\text{aq})}$ decreased to half of its original intensity in only 31 minutes and two new lines at 1.08 and -0.14 ppm appeared in the spectrum. The line at 1.08 ppm is assigned to $\text{MeHg}^+_{(\text{aq})}$ by comparison with the literature¹² whereas the line at -0.14 ppm is due to $\text{MeGa}^+_{(\text{aq})}$. The observed



formation of $\text{MeHg}^+_{(\text{aq})}$ instead of HgMe_2 is consistent with previously observed methylation reactions of mercury(II). Others⁹ have also observed that it is more difficult to methylate $\text{MeHg}^+_{(\text{aq})}$ than $\text{Hg}^{2+}_{(\text{aq})}$ due to the decreased electrophilic character of $\text{MeHg}^+_{(\text{aq})}$. It is significant to note that mercury(II) acetate is also methylated¹³ by $\text{Me}_2\text{Tl}(\text{MeCO}_2)$, another group 3 alkyl, to yield $\text{MeHg}^+_{(\text{aq})}$ and $\text{MeTl}^{+2}_{(\text{aq})}$.

Bis(diacetylmonoximeimino1,3propane)dimethylcobalt(III), $\text{Me}_2\text{Co}(\text{BDM}1,3\text{pn})$, methylates gallium(III) perchlorate and gallium(III) chloride in polar solvents. This reaction represents the first reported example of the formation of a dimethylgallium(III) species in a protic solvent. The stoichiometry of the reaction as shown by equation 4 is consistent with all UV titration data. In the UV titrations, absolute ethanol solutions of



$\text{Ga}(\text{ClO}_4)_3$ were added to ethanol solutions of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$. The linear decrease in the absorbance at 412 nm, characteristic of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$,¹⁰ as well as the increase in the absorbance at 470 nm, characteristic of the methylcobalt(III) product,¹⁰ $\text{MeCo}(\text{BDM1,3 pn})^+$, were used to determine the extent of reaction. A plot of the absorbance at 412 nm versus the mol ratio $\text{Ga}^{+3}/\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ had a distinct break at 0.532 mole of Ga^{+3} per mole of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ (Figure 1). The observation of only the absorbance at 470 nm¹⁰ at the end of the titration demonstrates the formation of $\text{MeCo}(\text{BDM1,3 pn})^+$ and precludes the possibility that both methyl groups are removed from cobalt.

The proposed stoichiometry of the $\text{Ga}^{+3}-\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ reaction and the identity of the products are also supported by ^1H NMR spectral data. The products observed after reaction were $\text{MeCo}(\text{BDM1,3 pn})^+$ and Me_2Ga^+ . The NMR spectrum of $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ in acetone is characterized by a sharp singlet at -0.16 ppm (referenced to benzene at 7.13 ppm) for the methyl groups bound to cobalt. This resonance disappeared as $\text{Ga}(\text{ClO}_4)_3$ was added and two new sharp lines at 0.51 and -0.26 ppm due to methyl groups of $\text{MeCo}(\text{BDM1,3 pn})^+$ and Me_2Ga^+ , respectively, appeared. The identity of the species responsible for the -0.26 ppm line, Me_2Ga^+ , was verified by examining the ^1H NMR spectrum of the product mixture after the addition of a solution of pure $\text{Me}_2\text{GaClO}_4$. The stoichiometry of the methylation reaction of gallium(III) by $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ and identity of the reaction products were independent of the solvent, ethanol, acetone or acetonitrile, and the gallium(III) reactant, $\text{Ga}(\text{ClO}_4)_3$ and $\text{Ga}(\text{NO}_3)_3$.

Gallium species other than simple solvated Ga^{+3} ions have also been shown to undergo methyl transfer reactions with $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ in acetone and ethanol solution. Anhydrous GaCl_3 dissolves in ethanol and acetone but

the exact nature of the solubilized species is unknown. Therefore, the gallium(III) solute¹⁴ will be referred to as $[\text{GaCl}_n]^{(3-n)+}$. These solutions react readily with $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ in a 1:2 stoichiometry to yield $\text{MeCo}(\text{BDM1,3 pn})^+$ and a dimethylgallium(III) product according to data from UV spectroscopic titrations and ^1H NMR studies. It is also significant that $[\text{GaCl}_n]^{(3-n)+}$ undergoes a faster methyl transfer reaction with Me_2Ga^+ in acetone than Ga^{+3} from $\text{Ga}(\text{ClO}_4)_3$ does in water. The intensity of the ^1H NMR line due to Me_2Ga^+ decreased to one half intensity in 112 hours in the presence of excess $[\text{GaCl}_n]^{(3-n)+}$ in acetone solution and a new line due to MeGa^{+2} appeared.

The methylcobalt(III) complex $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ is considered to be of high reactivity for the methylation of metal ions whereas methylcobalamin is significantly less reactive.¹⁰ Since Ga^{+3} reacted so readily with $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ to form Me_2Ga^+ , the reactivity of methylcobalamin toward $\text{Ga}(\text{ClO}_4)_3$ in aqueous solution was studied by UV titration experiments. However, no reaction occurred. The absorbance of the bands of methylcobalamin at 520 and 350 nm did not change significantly as an aqueous solution of $\text{Ga}(\text{ClO}_4)_3$ was added. Thus, it is unlikely that exceedingly toxic methylgallium species will be formed directly by methylcobalamin methylation in the aqueous environment.

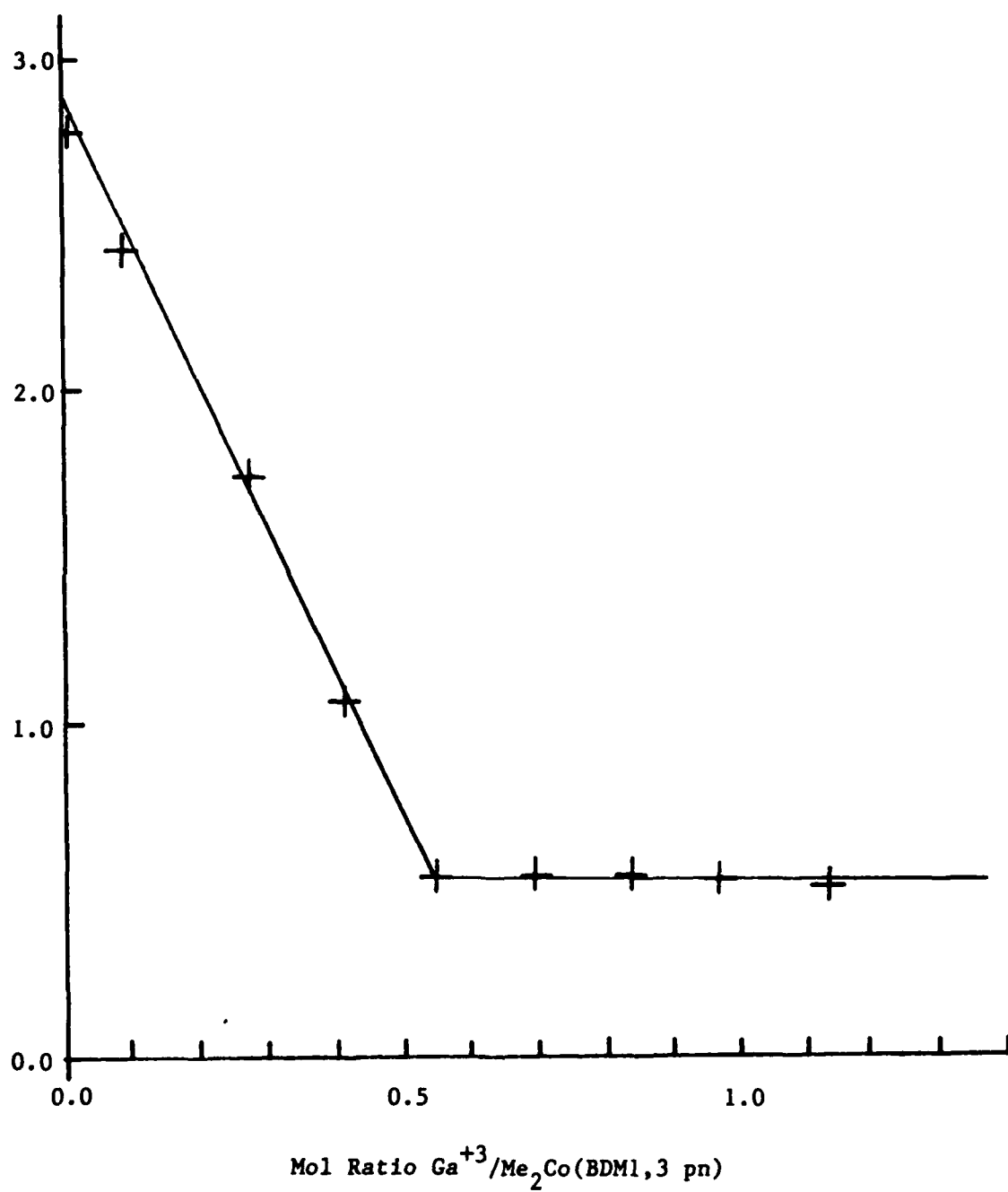
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Figure 1

Titration of $\text{Me}_2\text{Co}(\text{BDMl}, 3 \text{ pn})$ with $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$



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